

AD-A097 552 DEFENCE RESEARCH ESTABLISHMENT ATLANTIC DARTMOUTH (NO--ETC F/G 7/4
X-RAY FLUORESCENCE SPECTROMETRIC ANALYSIS OF WEAR METALS IN USE--ETC(U)
DEC 80 D E VEINOT
UNCLASSIFIED DREA-TM-80/J NL

DEFENCE RESEARCH ESTABLISHMENT ATLANTIC DARTMOUTH (NO--ETC F/G 7/4
X-RAY FLUORESCENCE SPECTROMETRIC ANALYSIS OF WEAR METALS IN USE--ETC(U)
DEC 80 D E VEINOT
DREA-TM-80/J NL

NL

UNCLASSIFIED

END
DATE
FILMED
DTIC

LEVEL II

UNLIMITED
DISTRIBUTION
ILLIMITÉE

285

DEFENCE RESEARCH ESTABLISHMENT
ATLANTIC

AD A 097552

DTIC
ELECTE
APR 9 1981
C

X-RAY FLUORESCENCE SPECTROMETRIC ANALYSIS
OF WEAR METALS IN
USED LUBRICATING OILS

DTIC FILE COPY



RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
CANADA

✓ D. R. E. A. TECHNICAL MEMORANDUM 80/J

81 4 09 022

DEFENCE RESEARCH ESTABLISHMENT ATLANTIC

9 GROVE STREET

P O BOX 1012
DARTMOUTH, N S
B2Y 3Z7

TELEPHONE
(902) 426-3100

CENTRE DE RECHERCHES POUR LA DÉFENSE ATLANTIQUE

9 GROVE STREET

C P 1012
DARTMOUTH, N E
B2Y 3Z7

**RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
CANADA**

DEFENCE RESEARCH ESTABLISHMENT ATLANTIC

2

DEFENCE RESEARCH ESTABLISHMENT
ATLANTIC

9 DARTMOUTH N.S.

D.R.E.A. TECHNICAL MEMORANDUM 80/J

14 DREA-TM-80/J

6
X-RAY FLUORESCENCE SPECTROMETRIC ANALYSIS
OF WEAR METALS IN
USED LUBRICATING OILS.

10 Dwight. E. Veinot

11 Dec 1980

12 18

DTIC
ELECTE
APR 9 1981
C

Approved by J. R. Brown A/Director / Technology Division

DISTRIBUTION APPROVED BY

J.R. Brown

CHIEF D.R.E.A.

RESEARCH AND DEVELOPMENT BRANCH
DEPARTMENT OF NATIONAL DEFENCE
CANADA

432761

DISTRIBUTION STATEMENT X
Approved for public release,
Distribution Unlimited

mt

ABSTRACT

→ An x-ray fluorescence spectrometric technique was developed for the direct determination of iron and copper wear metal concentrations in used lubricating oils from CH 124 "Sea King" helicopter engines. The x-ray fluorescence wear metal levels were compared to the atomic absorption wear metal levels determined on corresponding samples. In general, the x-ray fluorescence results indicated higher levels of wear metal contamination and also provided earlier indications of abnormal wear based on more pronounced changes in detected wear metal production than did the results obtained by atomic absorption analysis. ↙

| | |
|--------------------|--|
| Accession For | |
| NTIS GRA&I | <input checked="checked" type="checkbox"/> |
| DTIC TAB | <input type="checkbox"/> |
| Unannounced | <input type="checkbox"/> |
| Justification | |
| By _____ | |
| Distribution/ | |
| Availability Codes | |
| Dist | Avail and/or Special |
| A | |

RESUME

On a mis au point une technique de spectrométrie par fluorescence des rayons X pour déterminer directement les concentrations de poussières de fer et de cuivre dans les huiles usées des moteurs des hélicoptères CH 124 "Sea King". On a comparé les valeurs obtenues à l'aide de cette méthode avec celles obtenues par absorption atomique sur des échantillons correspondants. En général, les résultats obtenus par fluorescence des rayons X montraient des concentrations plus élevées de poussières métalliques contaminantes et permettraient de détecter plus tôt que l'analyse par absorption atomique une usure anormale d'après le changement plus marqué des quantités de poussières métalliques produites.

TABLE OF CONTENTS

| | <u>Page No.</u> |
|---------------------------|-----------------|
| ABSTRACT | ii |
| NOTATION | v |
| 1. INTRODUCTION | i |
| 2. EQUIPMENT | 2 |
| 3. PROCEDURE | 3 |
| 4. RESULTS AND DISCUSSION | 3 |
| 5. CONCLUSIONS | 4 |
| REFERENCES | 6 |
| TABLES | 7 |
| FIGURES | 10 |

NOTATION

| | |
|------|------------------------------------|
| SOAP | Spectrometric Oil Analysis Program |
| AAS | Atomic Absorption Spectrometric |
| XRFS | X-ray Fluorescence Spectrometric |
| °C | degrees centigrade |
| ml | millilitre |
| cps | counts per second |
| ppm | parts per million |
| Fe | iron |
| Cu | copper |
| KV | kilovolt |
| ma | milliamp |

1. INTRODUCTION

The Canadian Forces machinery health monitoring program is based on relating the internal condition of a machine to the concentration of various wear metals in used lubricating oil from the machine¹. At present, the Canadian Forces Spectrometric Oil Analysis Program (SOAP), utilizes atomic absorption spectrometric (AAS) techniques for determining wear metal levels in the used oils. The basic concept on which the program operates is that moving contact between oil lubricated metallic components is accompanied by friction which causes a transformation of the contacting surfaces into small particles (wear particles) which are deposited in the lubricating oil. The rate of increase in the production of these wear particles is an important indicator of the internal condition of the machine. It is used together with established guideline maximum wear metal levels in predicting incipient failure and the need for machinery overhaul; the object being to avoid catastrophic failure in service.

Although the AAS method of wear metal analysis has proven itself to be effective over many years of use, it suffers from the inherent drawback that in order to be detected, the wear metals must be dissolved in the used oil or present as finely divided particles. The probability that a wear metal particle will be detected decreases as the particle size increases, mainly because of two effects. Firstly, particles are not aspirated into the flame as efficiently as metals in solution and secondly, the flame may not have sufficient energy to atomize the particles. It is commonly accepted that particles greater than 5 micrometers in size escape detection. However, during the critical stages of abnormal wear, it is characteristic that both the quantity and size of the wear particles produced increase. Therefore, a potentially valuable source of information regarding internal condition during the most critical stages of wear is lost to the analyst. A further complication to the AAS method results from the requirement to reduce sample viscosity in order to achieve efficient aspiration of the sample into the flame by diluting with a low viscosity solvent. This is an important step in the analytical procedure which requires substantial attention and time to avoid sample preparation errors. Also, because of the equipment required for AAS analysis, the technique offers no potential for development as an on-line analysis technique.

It follows then, that a method which could be used to analyze the samples as received or could be adapted for

on-line analysis and which would be less sensitive to the size of wear particles than the AAS method, would offer the possibilities of both earlier and more positive indication of impending failure and would also reduce the possibility of errors resulting from sample preparation procedures.

This report describes an x-ray fluorescence spectrometric (XRFS) procedure that can be used to analyze used lubricating oils as received with increased probability of wear detection due to its ability to detect both metals in solution and particles of all sizes. The procedure has been used to measure iron and copper wear metal levels in used oils from CH 124 "Sea King" helicopter engines. The results obtained have been compared to the AAS results obtained on the same samples in order to evaluate the diagnostic capabilities offered by the XRFS method relative to those offered by the AAS method.

Iron and copper were chosen to illustrate the XRFS oil analysis procedure for several reasons. Iron and/or copper are the principle alloying elements in the majority of oil lubricated components in the T58-GE-8F engines. Therefore, accurate determination of the concentrations of these two elements in the used oil provides an effective means of condition monitoring. However, other elements such as silver, chromium, nickel, aluminum and magnesium have also been used effectively for condition monitoring by the AAS method. The XRFS procedure described does not provide adequate sensitivity for the determination of magnesium and aluminum. To do these elements at 1 ppm sensitivity requires analysis within a vacuum or helium filled chamber. Silver, chromium and nickel are seldom present at greater than 1 ppm but the procedure described could be employed to determine these elements if they were present at concentrations greater than 1 ppm. Lower level detection i.e., 0.1 ppm of these elements (especially silver) by a modified XRFS technique will be the subject of future work.

2. EQUIPMENT

A Philips PW 1410 manual/vacuum x-ray spectrometer equipped with a Philips PW 2182 rhodium side window x-ray tube was used for this work. The rhodium x-ray tube was powered by a Philips PW 1130 x-ray generator. Fluorescent x-rays from elements in the liquid oil samples were detected sequentially using tandemly operated scintillation and flow proportional counters. Ten percent methane in argon was used in the flow proportional detector. The x-ray processing equipment used

included a Philips PW 4280 amplifier analyzer, PW 1362 ratemeter, PW 4234 scaler and a PW 4260 timer.

3. PROCEDURE

The used lubricating oil samples were warmed to 70°C and shaken vigorously to ensure homogeneous distribution of the wear debris in the sample. Approximately a 10 ml portion of each sample was poured into a disposable plastic sample cup (Chemplex Industries, Cat. No. 1540) which was fitted with a thin (4 micrometer) polyester film (Somar Laboratories Inc., Cat. No. 3615-33) bottom window. A similar polyester window was then fitted to the top of the sample cup to eliminate spills when handling the samples.

The analysis conditions were optimized for both iron and copper based on a calculation of the figure of merit as described by Jenkins² using results obtained from a 100 ppm metal-in-oil standard. Calibration curves of x-ray response versus iron and copper wear metal concentrations were prepared using standards containing 0, 5, 10, 20, 50, 100, 200 and 500 ppm of each metal in synthetic MIL-L-23699B lubricating oil. During the analysis, the samples were spun at a rate of one revolution per second to minimize the effect of surface irregularities. Figure I shows the calibration curves from 0 to 500 ppm. The concentrations obtained by XRFS for iron and copper wear metal levels were compared to the iron and copper wear metal levels that were determined by the normal AAS procedure in corresponding samples. The absolute concentrations of iron and copper in the oil samples were determined by ashing weighed aliquots of each sample, dissolving the ash in acid and then determining the metal concentrations in the resulting aqueous solutions.

4. RESULTS AND DISCUSSION

X-ray response was linearly dependent on concentrations up to at least 500 ppm with a lower limit of detection of 1 ppm for both copper and iron. Figure I shows the calibration curves used for this work. The relatively high background levels shown in these curves are the result of high scattering of excitation source x-rays by the oil.

Table I shows a comparison of the XRFS and the AAS iron and copper wear metal levels found in successive samples of used oil from T58-GE-8F helicopter engines that were

considered to be operating normally. As shown by the four cases presented in Table I, both the AAS and XRFS results indicate low wear metal levels with negligible change in the concentrations determined in successive samples. Thus both techniques indicate normal operation. Note that in cases 2 and 3 the iron and copper concentrations obtained by XRFS analysis are higher than those obtained by the AAS analysis. Absolute concentrations of these metals, obtained by ashing a weighed aliquot of each sample, dissolving the ash in acid and determining iron and copper concentrations in the resulting aqueous solutions, validated the results obtained by XRFS analysis in all cases.

Table II shows a comparison of the XRFS and AAS wear metal levels found in successive samples of used oil from T58-GE-8F engines that were considered to be operating abnormally or that had failed. In all cases, the XRFS results show higher levels of wear metal contamination than the AAS results. In addition, they indicate a rising concentration at least one sample interval earlier than the AAS results and show, at the same time, a more pronounced and therefore more readily noticeable deviation from the levels indicative of normal wear. For example, referring to case 7, the AAS results indicate a stabilized iron concentration of 3 ppm, thus indicating normal operation. However, the XRFS results indicate a change in status with associated increased iron concentrations from the sample taken at 80.4 hours onwards until the engine was finally removed from service because large particles were discovered on the filter elements. The sample taken at 155.0 operating hours was not representative, probably because of a sampling error. Other cases shown in Table II also show the earlier and more evident failure prediction capability of XRFS wear metal analysis. The XRFS results obtained on these cases were also validated by the ashing procedure previously described.

5. CONCLUSIONS

The XRFS oil analysis procedure offers a simple and accurate means of determining copper and iron wear metal concentrations in used lubricating oils. Unlike the conventionally employed AAS method, this method provides accurate analytical results independent of the size of the wear particles. A comparison of the XRFS and AAS results indicates that for normally operating engines, both sets of results show close agreement. However, for abnormally operating engines the XRFS results show higher wear metal levels and a more pronounced change in concentration in successive samples. Thus the XRFS

procedure provides an earlier and more positive indication of impending failure. The XRFS results were found to be more accurate than the AAS results especially when contamination levels were high. In addition, the XRFS method does not require that the samples be diluted with low viscosity solvents thus eliminating one potential source of error and reducing sample preparation time. One additional advantage of the XRFS method is that with the appropriate equipment modifications, the basic concept could be applied to on-line analysis of the oil during service.

REFERENCES

1. C-05-005-008/AM-000, Aerospace Spectrometric Oil Analysis Program, 79-09-28.
2. Jenkins, Ron, An Introduction to X-Ray Spectrometry, Heydon and Son Ltd., 1974.

TABLE I
WEAR METAL LEVELS IN USED OIL
FROM NORMALLY OPERATING ENGINES

| <u>Case Number</u> | <u>Equipment Serial Number</u> | <u>Hours Since Oil Change</u> | <u>A.A.S.</u> | | <u>X.R.F.S.</u> | |
|------------------------|--|-----------------------------------|---------------------|---------------------|---------------------|---------------------|
| | | | <u>Fe (ppm)</u> | <u>Cu (ppm)</u> | <u>Fe (ppm)</u> | <u>Cu (ppm)</u> |
| 1 | 275115 | 6.0 | <1 | <1 | <1 | <1 |
| | | 9.1 | <1 | <1 | <1 | <1 |
| | | 11.4 | <1 | <1 | <1 | <1 |
| | | 11.9 | <1 | <1 | <1 | <1 |
| | | 42.2 | <1 | <1 | <1 | <1 |
| | | 69.3 | 1 | <1 | <1 | <1 |
| 2 | 275071 | 0.5 | <1 | <1 | 1 | 4 |
| | | 3.2 | <1 | <1 | 1 | 4 |
| | | 32.6 | <1 | <1 | 1 | 4 |
| 3 | 275006 | 7.0 | <1 | <1 | 2 | 3 |
| | | 33.1 | <1 | <1 | 3 | 4 |
| | | 57.7 | <1 | <1 | 3 | 4 |
| | | 81.9 | <1 | <1 | 3 | 4 |
| 4 | 275169 | 28.8 | 0 | <1 | <1 | <1 |
| | | 52.8 | 0 | <1 | <1 | <1 |
| | | 86.9 | 0 | <1 | <1 | <1 |
| | | 111.6 | 0 | <1 | <1 | <1 |

TABLE II
WEAR METAL LEVELS IN USED OILS
FROM ABNORMALLY OPERATING ENGINES

| <u>Case Number</u> | <u>Equipment Serial Number</u> | <u>Hours Since Oil Change</u> | <u>A.A.S.</u> | | <u>X.R.F.S.</u> | |
|------------------------|--|-----------------------------------|---------------------|---------------------|---------------------|---------------------|
| | | | <u>Fe (ppm)</u> | <u>Cu (ppm)</u> | <u>Fe (ppm)</u> | <u>Cu (ppm)</u> |
| 1 | 275100 | 24.1 | 0 | <1 | 2 | 3 |
| | | 53.7 | 0 | <1 | 4 | 3 |
| | | 79.3 | 4 | <1 | 9 | 3 |
| | | 105.5 | 5 | <1 | 9 | 3 |
| 2 | 275055 | 17.1 | 3 | <1 | 7 | 4 |
| | | 45.0 | 3 | <1 | 13 | 4 |
| | | <u>Failed</u> | 4 | <1 | 330 | 62 |
| 3 | 275041 | 113.6 | 2 | <1 | 8 | 3 |
| | | 129.3 | 2 | <1 | 8 | 3 |
| | | 142.4 | 1 | <1 | 8 | 3 |
| | | 150.9 | 2 | <1 | 19 | 4 |
| | | particles on filter | 2 | <1 | 19 | 4 |
| | | | | | | |
| 4 | 275119 | 99.6 | 1 | <1 | 7 | 2 |
| | | 111.9 | 2 | <1 | 8 | 2 |
| | | 126.6 | 2 | 2 | 17 | 2 |
| | | 139.8 | 8 | 2 | 34 | 7 |
| | | 147.9 | 8 | 2 | 42 | 7 |

(...Cont'd)

| <u>Case Number</u> | <u>Serial Number</u> | <u>Hours Since Oil Change</u> | <u>A.A.S.</u> | | <u>X.R.F.S.</u> | |
|------------------------|--------------------------|-----------------------------------|---------------------|---------------------|---------------------|---------------------|
| | | | <u>Fe (ppm)</u> | <u>Cu (ppm)</u> | <u>Fe (ppm)</u> | <u>Cu (ppm)</u> |
| 5 | 275170 | 12.3 | 1 | <1 | 20 | 1 |
| | | 24.4 | 1 | <1 | 20 | 1 |
| | | 39.3 | 2 | <1 | 35 | 1 |
| | | 54.7 | 2 | <1 | 45 | 2 |
| | | 70.0 | 2 | <1 | 50 | 2 |
| | | 82.5 | 2 | <1 | 85 | 2 |
| | | 95.9 | 3 | <1 | 115 | 3 |
| | | 108.6 | 4 | <1 | 192 | 3 |
| 6 | 275035 | 2.8 | 1 | <1 | 5 | 2 |
| | | 16.9 | 3 | <1 | 10 | 2 |
| | | 30.9 | 6 | <1 | 14 | 2 |
| | | 43.9 | 11 | <1 | 28 | 2 |
| | | 55.6 | 10 | <1 | 35 | 2 |
| | | 61.4 | 12 | <1 | 62 | 2 |
| | | 64.1 | 16 | <1 | 85 | 3 |
| | | 65.1 | 19 | <1 | 125 | 3 |
| | | 65.6 | 19 | <1 | 130 | 3 |
| 7 | 275151 | 80.4 | 2 | <1 | 14 | <1 |
| | | 106.3 | 2 | <1 | 26 | <1 |
| | | 121.1 | 3 | <1 | 31 | <1 |
| | | 155.0 | <1 | <1 | <1 | <1 |
| | | 176.6 | 3 | <1 | 72 | <1 |
| | | 202.2 | 3 | <1 | 76 | <1 |
| | | 208.2 | 3 | <1 | 134 | <1 |

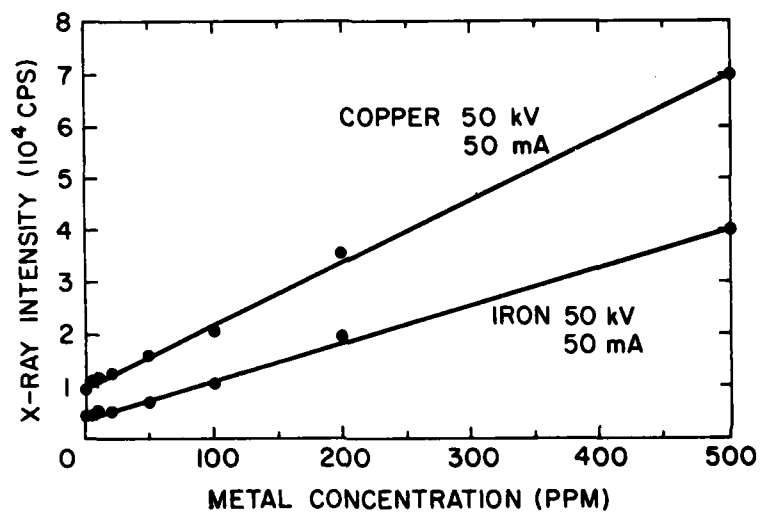


Figure 1: Calibration curves for copper and iron in MIL-L-23699B lubricating oil.

UNCLASSIFIED

Security Classification

| DOCUMENT CONTROL DATA - R & D | | |
|--|---|--|
| (Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified) | | |
| 1. ORIGINATING ACTIVITY Defence Research Establishment Atlantic, Dockyard Laboratory, FMO Halifax, N.S. B3K 2X0 | | 2a. DOCUMENT SECURITY CLASSIFICATION Unclassified |
| | | 2b. GROUP |
| 3. DOCUMENT TITLE X-ray Fluorescence Spectrometric Analysis of Wear Metals in Used Lubricating Oils | | |
| 4. DESCRIPTIVE NOTES (Type of report and inclusive dates) Tech Memo | | |
| 5. AUTHOR(S) (Last name, first name, middle initial) Veinot, Dwight E. | | |
| 6. DOCUMENT DATE December 1980 | 7a. TOTAL NO. OF PAGES 17 | 7b. NO. OF REFS 2 |
| 8a. PROJECT OR GRANT NO. | 9a. ORIGINATOR'S DOCUMENT NUMBER(S) DREA TECHNICAL MEMORANDUM 80/J | |
| 8b. CONTRACT NO. | 9b. OTHER DOCUMENT NO.(S) (Any other numbers that may be assigned this document) | |
| 10. DISTRIBUTION STATEMENT | | |
| 11. SUPPLEMENTARY NOTES | 12. SPONSORING ACTIVITY Defence Research Establishment Atlantic 9 Grove Street Dartmouth, N.S. B2Y 3Z7 | |
| 13. ABSTRACT An x-ray fluorescence spectrometric technique was developed for the direct determination of iron and copper wear metal concentrations in used lubricating oils from CH 124 "Sea King" helicopter engines. The x-ray fluorescence wear metal levels were compared to the atomic absorption wear metal levels determined on corresponding samples. In general, the x-ray fluorescence results indicated higher levels of wear metal contamination and also provided earlier indications of abnormal wear based on more pronounced changes in detected wear metal production than did the results obtained by atomic absorption analysis. | | |

 (1515
 14-470

KEY WORDS

X-ray Fluorescence

Analysis

Wear metals

Oils

INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the organization issuing the document.
- 2a. **DOCUMENT SECURITY CLASSIFICATION:** Enter the overall security classification of the document including special warning terms whenever applicable.
- 2b. **GROUP:** Enter security reclassification group number. The three groups are defined in Appendix 'M' of the DRB Security Regulations.
3. **DOCUMENT TITLE:** Enter the complete document title in all capital letters. Titles in all cases should be unclassified. If a sufficiently descriptive title cannot be selected without classification, show title classification with the usual one-capital-letter abbreviation in parentheses immediately following the title.
4. **DESCRIPTIVE NOTES:** Enter the category of document, e.g. technical report, technical note or technical letter. If appropriate, enter the type of document, e.g. interim, progress, summary, annual or final. Give the inclusive dates when a specific reporting period is covered.
5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the document. Enter last name, first name, middle initial. If military, show rank. The name of the principal author is an absolute minimum requirement.
6. **DOCUMENT DATE:** Enter the date (month, year) of Establishment approval for publication of the document.
- 7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.
- 7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the document.
- 8a. **PROJECT OR GRANT NUMBER:** If appropriate, enter the applicable research and development project or grant number under which the document was written.
- 8b. **CONTRACT NUMBER:** If appropriate, enter the applicable number under which the document was written.
- 9a. **ORIGINATOR'S DOCUMENT NUMBER(S):** Enter the official document number by which the document will be identified and controlled by the originating activity. This number must be unique to this document.
- 9b. **OTHER DOCUMENT NUMBER(S):** If the document has been assigned any other document numbers (either by the originator or by the sponsor), also enter this number(s).
10. **DISTRIBUTION STATEMENT:** Enter any limitations on further dissemination of the document, other than those imposed by security classification, using standard statements such as:
 - (1) "Qualified requesters may obtain copies of this document from their defence documentation center."
 - (2) "Announcement and dissemination of this document is not authorized without prior approval from originating activity."
11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.
12. **SPONSORING ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring the research and development. Include address.
13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document, even though it may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall end with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (TS), (S), (C), (R), or (U).

The length of the abstract should be limited to 20 single-spaced standard typewritten lines; 7 1/4 inches long.
14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a document and could be helpful in cataloging the document. Key words should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical content.

